

Chemistry and cooling in metal-free and metal-poor gas

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Abstract. I summarize four of the most important areas of uncertainty in the study of the chemistry and cooling of gas with zero or very low metallicity. These are: i) the importance and effects of HD cooling in primordial gas; ii) the importance of metal-line and dust cooling in low metallicity gas; iii) the impact of the large uncertainties that exist in the rate coefficients of several key reactions involved in the formation of H_2 ; and iv) the effectiveness of grain surface chemistry at high redshifts.

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INTRODUCTION

Astrochemistry – chemistry in an astrophysical context – is a huge subject, owing to the extremely large number of reactions that are possible, and the complexity of the resultant reaction networks. For instance, the reaction sets used to study the chemistry of local molecular clouds typically include more than 300 reactants and more than 4000 reactions simply to represent the gas-phase chemistry. The inclusion of grain surface chemistry makes things even more complex. However, when studying the formation of the earliest generations of stars, our primary concern is to properly model the thermal behaviour of the gas, as this strongly influences its hydrodynamical evolution. We can therefore focus our attention solely on the chemistry of the major coolants, allowing us to sidestep much of the chemical complexity, and to include only those reactants and reactions in our model that are necessary for understanding the thermal evolution of the gas.

An influential study of the chemistry of metal-free gas performed along these lines by [1] demonstrated that out of the many hundreds of possible reactions, only 28 were needed to accurately model the thermal evolution of the gas over a wide range of parameter space. Subsequently, other authors have added a few additional reactions to this simplified model that are very important in some circumstances (e.g. HD formation and destruction, [2]; three-body H_2 formation, [3]), but not in others.

A similar approach has recently been applied to metal-poor gas by [4] and [5], under the assumption that the dominant coolants in metal-poor gas are the same as those in the local atomic and molecular ISM (i.e. carbon, oxygen and silicon fine-structure lines, CO and H_2O rotational and vibrational emission, and dust). In this case, the required number of reactions is an order of magnitude larger than in the metal-free case, but is still small enough to be computationally tractable.

Nevertheless, despite our success at identifying the

most important reactions and hence simplifying the treatment of the chemistry to the point where it can be modelled self-consistently within large, three-dimensional hydrodynamical simulations, a number of issues remain unresolved. In this contribution, I briefly discuss a few of what I consider to be the most important areas of ongoing uncertainty or confusion in the study of the chemistry and cooling of metal-free and metal-poor gas.

PROBLEM 1: THE ROLE OF HD COOLING

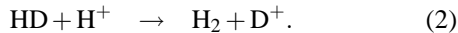
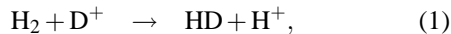
At temperatures $200 < T < 10000$ K in a metal-free gas (or in low-density metal-poor gas; [6]), molecular hydrogen is the most abundant molecular species and is also the dominant coolant. However, at low temperatures, H_2 cooling becomes increasingly ineffective, owing to the large energy difference that exists between its $J = 0$ and $J = 2$ rotational levels, and the fact that the lower energy $J = 1 \rightarrow 0$ transition is strongly forbidden. At these low temperatures, HD cooling is far more effective, in the sense that the cooling rate per molecule of HD is much larger than the cooling rate per molecule of H_2 . However, the small size of the cosmic D/H ratio means that in general HD is far less abundant than H_2 . Because of this, for a long time it was unclear whether or not HD was ever an important coolant in practice. In the past few years, however, considerable effort has been devoted to exploring the consequences of HD cooling in the early Universe, and its role has now become much clearer.

In [7], the impact of HD cooling in the first star-forming protogalaxies was examined, and it was shown that given a D/H ratio consistent with observationally measured values, HD cooling was unimportant. More recently, the role of HD cooling within a wider range of protogalaxies was examined ([8]), with the conclusion that in very low mass protogalaxies ($M < 3 \times 10^5 M_\odot$),

HD cooling may be marginally important.

These calculations typically adopted an initial temperature and chemical composition for the gas consistent with the values applicable to the undisturbed IGM. However, other studies that start with initially ionized gas (e.g. [9, 10]) find that in this case, HD cooling *is* important, and that it can often cool the gas all the way down to the temperature floor set by the CMB.

Why do these two sets of calculations differ so much on the importance of HD? The answer lies in the low temperature chemistry of the HD molecule. In most circumstances, its formation and destruction are dominated by the ion-neutral exchange reactions:



Reaction 1 is exothermic, but reaction 2 is endothermic by 462 K ([11]). As a result, at low gas temperatures, considerable chemical fractionation occurs: the equilibrium value of the HD/H₂ ratio is enhanced over the cosmic D/H ratio by a factor $\sim e^{462/T}$. The effect of this on the cooling of the gas is illustrated in Figure 1, where I plot the cooling rate of the gas as a function of temperature for gas with $n = 100 \text{ cm}^{-3}$ and $x(\text{H}_2) = 10^{-3}$, and where $x(\text{HD})/x(\text{H}_2)$ is calculated assuming that reactions 1 and 2 have reached equilibrium. In practice, fractionation may not proceed fully to equilibrium owing to the depletion of the necessary D⁺ ions from the gas by recombination, so this plot should be regarded as giving an upper limit on the effectiveness of HD cooling at this density. Figure 1 demonstrates that at $T \sim 150 \text{ K}$, the increase in the HD abundance due to fractionation more than offsets the decrease in the H₂ and HD cooling rates per molecule. Consequently, gas that can cool to this critical temperature will begin to cool even more effectively, and thus can easily reach temperatures as low as T_{CMB} . The critical temperature that must be reached for HD cooling to take over in this fashion varies with n , but is never larger than 250 K, and exceeds 200 K only for gas with $n > 10^4 \text{ cm}^{-3}$.

It is now straightforward to explain why HD cooling becomes important in gas cooling from an initially highly ionized state, but not for gas cooling from a low-ionization state. In the former case, it has long been recognised that the out-of-equilibrium nature of hydrogen recombination in the cooling gas leads to enhanced production of H₂. As a result, gas cooling from a high-ionization state can reach a lower temperature than gas cooling from a low-ionization state. Although the temperature difference is not large, it turns out that in the former case, the gas can usually cool to T_{crit} , at which point HD takes over, while in the latter case it falls somewhat short, typically never cooling below $T \sim 200 \text{ K}$.

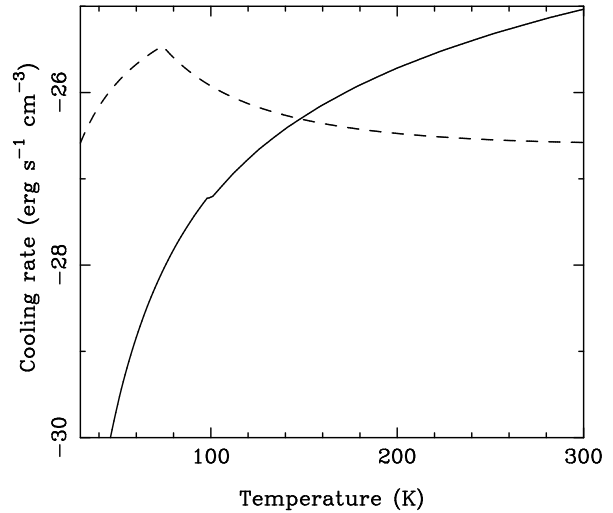


FIGURE 1. Cooling rates of H₂ (solid line) and HD (dashed line) in a gas with atomic hydrogen number density $n_{\text{H}} = 100 \text{ cm}^{-3}$. The fractional H₂ abundance is fixed at $x(\text{H}_2) = 10^{-3}$, while the HD/H₂ ratio, $x(\text{HD})/x(\text{H}_2)$, is calculated assuming that reactions 1 and 2 have reached equilibrium. The maximum abundance of HD is constrained to be no larger than the total deuterium abundance, here taken to be $x(\text{D}, \text{tot}) = 2.6 \times 10^{-5}$. This constraint is responsible for the sudden downturn in the HD cooling rate at low T .

This explanation accounts for the differences in behaviour observed in previous numerical simulations with different initial conditions, but also prompts a couple of further questions. First, what effect does the presence of an ultraviolet background in the Lyman-Werner bands of H₂ have on the ability of the gas to cool below T_{crit} ? Most previous simulations that include the effects of HD cooling have assumed that the ultraviolet background is zero, or at least is too small to be significant. Recently, however, the impact of a Lyman-Werner background on the effectiveness of HD cooling was investigated in [12] using a one-zone chemical model. This investigation suggests that if the field strength is greater than $3 \times 10^{-22} \text{ erg s}^{-1} \text{ cm}^{-2} \text{ Hz}^{-1} \text{ sr}^{-1}$, then the gas never cools below 200 K, and so HD cooling never becomes important. However, this calculation suffers from the problem – common to all one-zone models – that the dynamical evolution is not solved for self-consistently with the thermal evolution. Further investigation of this issue using a proper hydrodynamical approach would be extremely useful.

Second, does the extra cooling at low temperatures provided by the HD actually promote fragmentation? Judging by recent work (e.g. [10]), the answer is no: the additional cooling reduces the fragment mass scale, but despite this only a single fragment forms in each halo. However, the sharp rise in the cooling rate at $T <$

T_{crit} apparent in Figure 1 suggests that HD cooling may render the gas thermally unstable in some circumstances, which would tend to promote fragmentation.

PROBLEM 2: THE IMPORTANCE OF METALS

One of the most important unsolved problems in the study of star formation in very low metallicity gas is the role that cooling from gas-phase metals and dust grains plays in determining the stellar IMF. A popular hypothesis (introduced in [13]) holds that it is the enrichment of the star-forming gas with metals to a level greater than a critical metallicity Z_{crit} that brings about a transformation in the IMF from one dominated by massive stars to one more closely resembling the standard Salpeter IMF. The causal link between metal enrichment and the formation of lower mass stars is the greater effectiveness of metals as coolants (particularly at low temperature) compared to H_2 , which is supposed to enable the gas to gravitationally fragment down to much smaller mass scales.

Two different forms of metal-related cooling have attracted considerable attention: fine-structure cooling from C and O (and in some cases also Si and Fe; [14]), which is effective primarily at densities $n < 10^6 \text{ cm}^{-3}$ [13, 14, 15, 16], and dust cooling, which is effective at much higher densities [17, 18, 19, 20].

The effectiveness of fine-structure cooling at promoting fragmentation remains highly uncertain. The original simulations of [13] found fragmentation at $Z = 10^{-3} Z_{\odot}$ but not at $Z = 10^{-4} Z_{\odot}$, implying that $10^{-4} < Z_{\text{crit}} < 10^{-3} Z_{\odot}$. However, these simulations did not include the effects of H_2 cooling. Very similar simulations have recently been performed that do include H_2 cooling ([21]). In this case, fragmentation occurs even in runs with $Z = 0$, suggesting that the fragmentation seen in this type of simulation owes more to the choice of initial conditions than to metal-enrichment. Furthermore, simulations performed using alternative initial conditions in which the gas is hot and ionized ([21]) find no fragmentation at $Z \leq 10^{-3} Z_{\odot}$, whereas simulations by [16], performed using yet another set of initial conditions, *do* find fragmentation at $Z = 10^{-3} Z_{\odot}$. The logical conclusion to be drawn from these contradictory results is that whether or not metal-enriched gas fragments depends to a large extent on its initial state, and that without a better understanding of this, one cannot be certain about the importance of fine-structure cooling in driving fragmentation.

In the case of dust cooling, recent hydrodynamical simulations (described in [19], [20] and elsewhere in these proceedings) find that the gas readily fragments following the onset of dust cooling, provided that the available dust surface area per unit gas mass exceeds one

part in 10^5 of the value in solar metallicity gas. Although the simulations of [19], which consider the special case of gas with zero angular momentum, find only limited fragmentation, the simulations of [20], which consider the more general case of non-zero angular momentum, find a high level of fragmentation, with ~ 100 distinct fragments formed within only a few hundred years of the formation of the first object.

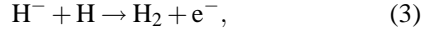
Nevertheless, despite these recent results, a number of serious questions remain. To begin with, both sets of simulations were performed using a tabulated equation of state, based on the thermal evolution of the gas found in one-zone models of low-metallicity protostellar collapse (e.g. [18]). However, one-zone models of this type do not self-consistently couple the thermal and dynamical evolution of the gas, and also cannot properly account for effects such as rotation. Conclusions based on one-zone models of collapse in metal-free gas have in the past proved to be highly misleading (see e.g. the discussion in [22]). Moreover, by using a tabulated equation of state, we implicitly assume that the gas temperature adjusts instantaneously to any changes in density; in practice, such changes are not instantaneous, but instead take place over a thermal timescale. It is possible that by making this implicit assumption, we are overestimating the propensity of the gas to fragment. Work aimed at clarifying these issues by solving the full thermal energy equation self-consistently within the hydrodynamical simulations is currently ongoing.

The other major concern about the current results is that they do not take into account feedback in the form of radiation from the accretion shocks surrounding the newly formed protostars. In local star-forming regions, this form of feedback may play a crucial role in stabilizing massive cores against sub-fragmentation ([23]), and so its effects should clearly also be included in the high redshift simulations. However, there are reasons to believe that its effects will be far less significant in a high-redshift, low-metallicity context. For one thing, the gas in these low-metallicity cores that cools rapidly and fragments is typically not optically thick, and so will absorb only a fraction of the radiation emitted by the accreting protostars. For another, the temperature of the dust in these objects is very much higher than in local star-forming regions ($T_d \sim 200 \text{ K}$ at the relevant densities, compared to $T_d \sim 10 \text{ K}$ locally), and so a much higher energy input is required to significantly alter the temperature of the gas. For these reasons, it seems unlikely that the inclusion of feedback will significantly alter the outcome of the simulations, but this expectation must nevertheless still be properly tested.

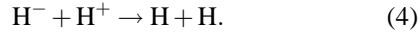
PROBLEM 3: RATE COEFFICIENT UNCERTAINTIES

Our ability to construct accurate models of the chemical evolution of metal-free or metal-poor gas is constrained by the level of accuracy to which the rate coefficients of the key chemical reactions have been determined. Most of the important reactions involved in the chemistry of H_2 and HD have well-determined rate coefficients ([1], [24]). However, there are a few important exceptions.

Two of these exceptions are the associative detachment of H^- with H

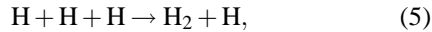


and the mutual neutralization of H^- with H^+



The available experimental and theoretical data on the low temperature ($T < 10^4$ K) behaviour of these two reactions is summarized in [25]. In both cases, the rate coefficients are uncertain by at least a factor of a few. In gas with a low fractional ionization, this uncertainty is unimportant, as reaction 3 occurs at a much faster rate than reaction 4, regardless of which of the possible values are selected for the two rate coefficients. In gas recombining from an initially ionized state, on the other hand, the uncertainties in reactions 3 and 4 combine to render the H_2 abundance uncertain by as much as an order of magnitude at some points during the chemical evolution of the gas. Some possible consequences of this were also explored in [25].

Another example is the large uncertainty that exists in the rate coefficient of the three-body H_2 formation reaction



the dominant source of H_2 in gas at densities $n > 10^8 \text{ cm}^{-3}$. In Figure 2, I show a selection of rate coefficients quoted in the literature for this reaction. The corresponding numerical values and references are listed in Table 1. This compilation includes one new rate coefficient (F), presented here for the first time. This was computed using the same detailed balance approach as in [26], but illustrates the effect of using an H_2 collisional dissociation rate taken from [27] in place of the rate from [28] used in [26].

It is clear from Figure 2 that although there is reasonable agreement between many of the rates at 5000 K, there is a substantial uncertainty in the rate in the temperature range $200 < T < 2000$ K relevant for population III star formation. Moreover, there is no sign that the rates are converging: two of the most recent determinations (A and D) are the two most widely discrepant rates.

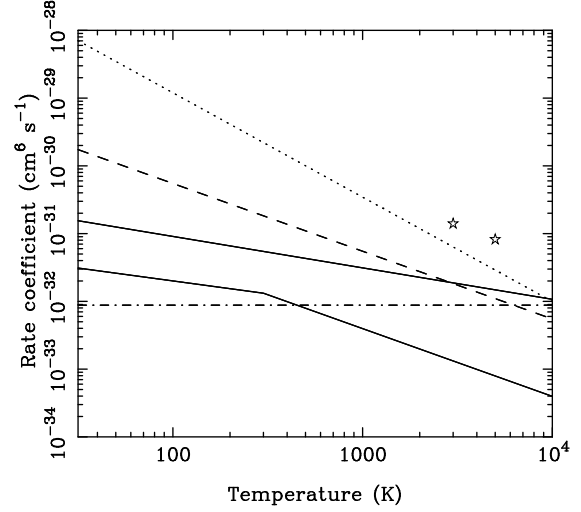


FIGURE 2. Three-body H_2 formation rate coefficients, plotted as a function of temperature. Key: A – lower solid line; B – dashed line; C – dot-dashed line; D – dotted line; E – star symbols; F – upper solid line.

TABLE 1. Rate coefficients for three-body H_2 formation

ID	Rate coefficient ($\text{cm}^6 \text{ s}^{-1}$)	Reference
A	$1.14 \times 10^{-31} T^{-0.38}$	$T \leq 300 \text{ K}$ [3]
	$3.9 \times 10^{-30} T^{-1.0}$	$T > 300 \text{ K}$
B	$5.5 \times 10^{-29} T^{-1.0}$	[29]
C	8.8×10^{-33}	[30]
D	$1.44 \times 10^{-26} T^{-1.54}$	[26]
E	1.4×10^{-31}	$T = 3000 \text{ K}$ [31]
	8.2×10^{-32}	$T = 5000 \text{ K}$
F	$7.7 \times 10^{-31} T^{-0.464}$	This work

The n^3 density dependence of the three-body H_2 formation process ensures that in collapsing primordial protostellar cores, the gas will rapidly become fully molecular at high densities, regardless of the rate coefficient adopted. However, the choice of rate coefficient will strongly influence the three-body H_2 formation heating rate, which is a major energy input into the gas at these densities, and may therefore also affect the further dynamical evolution of the gas. Simulations aimed at exploring the consequences of this uncertainty are currently in progress.

PROBLEM 4: GRAIN SURFACE CHEMISTRY

The key role that dust grains play in the chemistry of molecular gas in the Milky Way and in other local galaxies has been understood for more than 40 years. Very few

of the H_2 molecules in these systems were formed in the gas phase via the H^- or H_2^+ pathways that are so important in primordial gas. Instead, most were formed by reactions between hydrogen atoms adsorbed on the surface of interstellar dust grains. Moreover, H_2 is far from the only molecule that can form in this manner.

However, the importance of grain surface chemistry at high redshift remains an open question. There are two key issues. The first is that the amount of dust present in high redshift, low metallicity systems is not well constrained. A number of calculations have been performed that explore the formation of dust grains in high-redshift supernova remnants produced by metal-free progenitors ([32, 33, 34, 35, 36]), but the results of these calculations do not agree on the details of the resulting grain size distribution, and so the available grain surface area per unit gas mass remains uncertain.

The second key issue is the efficiency of molecule formation on high redshift dust grains. On local dust grains, most chemistry occurs through the interaction of van der Waals bonded (or ‘physisorbed’) atoms. The evaporation timescale for these atoms is typically orders of magnitude longer than the accretion timescale, and so the atoms have plenty of time in which to react. At high z , however, the dust grains are warmer, owing to the effects of heating by the CMB, and so the evaporation timescales, which depend exponentially on T_{dust} , are vastly smaller. For important atoms such as H, C or O, this means that $t_{\text{evap}} \ll t_{\text{acc}}$, and so the likelihood of there being more than a single atom physisorbed on a given grain at any given time is extremely small. Taken at face value, this implies that the efficiency of molecule formation on high redshift dust grains should be extremely small.

If one applies a similar argument to warm dust in local photodissociation regions, then one predicts a similar outcome: molecule formation, and in particular the formation of H_2 , should be extremely inefficient there. However, this conclusion conflicts with observationally-derived constraints on the H_2 formation rate in these regions, suggesting that some or all of the H_2 formed in these regions is formed from H atoms that are chemically bonded (or ‘chemisorbed’) to the surface of the grains ([37]). A detailed model for the formation of H_2 on grains that have both physisorption and chemisorption binding sites has recently been constructed by [38] and applied to the question of high-redshift H_2 formation by [39]. The results of this model suggest that once chemisorption is taken into account, H_2 formation remains efficient even at very high redshifts. However, this model is not without its critics (e.g. [40]), and as yet no similar modelling effort has been completed for the formation of any species other than H_2 , although work along these lines is currently under way.

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